XIII. *An Account of Experiments made by Mr.* JOHN Mc NAB, *at* Albany Fort, Hudſon's Bay, *relative to the Freezing of Nitrous and Vitriolic Acids. By* Henry Cavendiſh, *Eſq. F. R. S. and A. S.*

Read February 28, 1788.

FROM the experiments made by Mr. Mc NAB, of which I gave an account in the LXXVIth Volume of the Philoſophical Tranſactions, p. 241. it appeared, that ſpirit of nitre was ſubject, not only to what I call the aqueous congelation, namely, that in which it is chiefly, and perhaps intirely, the watery part which freezes, but alſo to another kind, in which the acid itſelf freezes, and which I call the ſpirituous congelation. When its ſtrength is ſuch as not to diſſolve ſo much as $\frac{243}{1000}$ of its weight of marble, or when its ſtrength is leſs than ,243, as I call it for ſhortneſs, it is liable to the aqueous congelation ſolely; and it is only in greater ſtrengths that the ſpirituous congelation can take place. This ſeems to be performed with the leaſt degree of cold when the ſtrength is ,411, in which caſe the freezing point is at $-1°\frac{1}{2}$. When the acid is either ſtronger or weaker, it requires a greater degree of cold; and in both caſes the frozen part ſeems to approach nearer to the ſtrength of ,411 than the unfrozen part. The freezing points, anſwering to different degrees of ſtrength, ſeemed to be as follows.

Strength.

Strength.	Freezing point.	
,54	$-31\frac{1}{2}$°	spirituous congelation.
,411	$-1\frac{1}{2}$°	spirituous congelation.
,38	$-45\frac{1}{4}$°	spirituous congelation.
,243	$-44\frac{1}{4}$°	aqueous congelation.
,21	-17°	aqueous congelation.

As ſome of theſe properties, however, were deduced from reaſoning not ſufficiently eaſy to ſtrike the generality of readers with much conviction, Mr. Mc NAB was deſired to try ſome more experiments to aſcertain the truth of it; which he was ſo good as to undertake, and has executed them with the ſame care and accuracy as the former.

For this purpoſe, I ſent him ſome bottles of ſpirit of nitre of different ſtrengths, and he was deſired to expoſe each of theſe liquors to the cold till they froze; then to try their temperature by a thermometer; afterwards to keep them in a warm room till the ice was almoſt melted, and then again expoſe them to the cold, and, when a conſiderable part of the acid had frozen, to try the temperature a ſecond time; then to decant the unfrozen part into another bottle, and ſend both parts back to England, that their ſtrength might be examined.

The intent of this ſecond expoſure to the cold was as follows. Spirit of nitre bears, like other liquors, to be cooled greatly below its freezing point without freezing: then the congelation begins ſuddenly; the liquor is filled with fine ſpicula of frozen matter, and the ice becomes ſo looſe and porous, that, if the proceſs be continued long enough for a conſiderable portion of the acid to congeal, ſcarce any of the fluid part can be decanted: whereas, if it be heated in this ſtate till the frozen part is almoſt, but not intirely, melted, and

and be again expoſed to the cold, as the liquor is then in contact with the congealed matter, it begins to freeze as ſoon as it arrives at the freezing point, and the ice becomes much more ſolid and compact.

The intent of decanting the fluid part, and ſending both parts back, that their ſtrength might be determined, was partly to examine the truth of the ſuppoſition laid down in my former Paper, that the ſtrength of the frozen part approaches nearer to ,411 than that of the unfrozen; but it is alſo a neceſſary ſtep towards determining the freezing point anſwering to a given ſtrength of the acid; for as the frozen part is commonly of a different ſtrength from the unfrozen, the ſtrength of the fluid part, and the cold neceſſary to make it freeze, is continually altering during the progreſs of the congelation. In conſequence of this, the temperature of the liquor is not that with which the frozen part congealed; but it is that neceſſary to make the remainder, or the fluid part, begin to freeze, or, in other words, it is the freezing point of the fluid part. This is the reaſon that a thermometer, placed in ſpirit of nitre, continually ſinks during the progreſs of congelation; which is contrary to what is obſerved in pure water, and other fluids in which no ſeparation of parts is produced by freezing.

Moreover, from the above-mentioned experiments of Mr. M^c^ NAB it appeared, that oil of vitriol, as well as ſpirit of nitre, is ſubject to the ſpirituous congelation; but it ſeemed uncertain, whether, like the latter, it had any point of eaſieſt freezing, or whether it did not uniformly freeze with leſs cold as the ſtrength increaſed. For this reaſon, ſome bottles of oil of vitriol, of different ſtrengths, were ſent, which he was deſired to try in the ſame manner as the former. This point, indeed, has ſince been determined by Mr. KEIR, who has

ſhewn

ſhewn that oil of vitriol has a ſtrength of eaſieſt freezing; and that at that point a remarkably ſlight degree of cold is ſufficient for its congelation.

The reſult of Mr. Mc NAB's experiments on the nitrous acid is given in the following table.

N°	Decanted part.		Undecanted part.		Strength of the whole maſs.	Strength before ſent.	Freezing point by firſt method.	Freezing point by ſecond method.
	Quantity.	Strength.	Quantity.	Strength.				
6	– –	– –	– –	– –	– –	,561	−41,6	– –
7	1410	,445	2137	,435	,439	,437	+*1,7	− 3,8
8	1658	,390	1940	,422	,407	,408	− 3,5	− 4
9	1368	,353	2438	,416	,393	,391	− 4,5	−11
10	2206	,343	1920	,373	,357	,357	−12,5	−13,8
11	3620	,310	602	,381	,320	,320	−22,5	−23
12	2155	,276	1494	,293	,283	,280	−39,1	−40,3
13	1618	,241	1961	,235	,238	,238	−34	−32

The firſt column contains the numbers by which Mr. Mc NAB has diſtinguiſhed the different bottles. The ſecond and third columns contain the quantity and ſtrength of the decanted part of the liquor; and the fourth and fifth ſhew the quantity and ſtrength of the undecanted part of the liquor. The ſixth column gives the ſtrength of both parts put together, or the ſtrength of the whole maſs; and the ſeventh is the ſtrength of the ſame acid, as it was determined before it was ſent to Hudſon's Bay. The ſtrengths of the decanted and undecanted parts were found by ſaturating the liquor returned home with marble; and that of the whole maſs was inferred by computation from the quantity and ſtrength of the decanted and undecanted parts; and as the ſtrength thus inferred never differs from that determined before the liquors were ſent to Hudſon's Bay by more than $\frac{1}{100}$ part of the

whole, it is not likely that the ſtrengths of the decanted and undecanted parts here ſet down ſhould differ from the truth by much more than that quantity.

The eighth column contains the freezing points found in the firſt method, or the temperature of the liquors after the haſty congelation which took place on expoſing them to the cold without any frozen matter in them; and the ninth contains their temperature after the more gradual congelation which took place when they were cooled with ſome frozen matter in them; and as the unfrozen part of the acid was decanted immediately after the temperature had been obſerved, it follows, that this column ſhews the true freezing points of the decanted liquors. In like manner the eighth column ſhews the freezing points of that part of the liquor which remained fluid in the firſt manner of trying the experiment; but as the ſtrength of this part was not determined, the preciſe ſtrengths to which theſe freezing points correſpond are unknown. Thus much, however, is certain, that theſe points muſt be below thoſe of the whole maſs, and in all probability muſt be above thoſe of the decanted liquor; as there is great reaſon to think, that the quantity of frozen matter was always leſs, and conſequently the ſtrength of the fluid part differed leſs from that of the whole maſs, in the firſt way of trying the experiment than in the ſecond.

Before I draw any concluſions from theſe experiments, it will be proper to take notice of ſome particularities which occurred in trying them.

N° 6. was made to congeal by a freezing mixture of ſnow and diluted oil of vitriol. By the time the acid was cooled to $-42°$, icy filaments were formed on the inſide of the phial above the acid. Ten minutes after, the acid being cooled one

degree

degree more, the phial was taken out and agitated. This mixed the icy filaments with the acid, and made it freeze, which it ſeems not to have done before, in conſequence of which its temperature roſe to $-41°\frac{1}{2}$. After having melted the greateſt part of theſe filaments, and again expoſed it to the freezing mixture, ſome ſnow accidentally fell into the acid, and made an uncertainty in the freezing point, for which reaſon it is not ſet down. But as it is evident, that the quantity of congealed matter in the firſt experiment was exceſſively ſmall, the ſtrength of the unfrozen part could not differ ſenſibly from that of the whole maſs, and therefore $-41°\frac{1}{2}$ is the true freezing point that anſwers to the ſtrength of ,561.

It is remarkable, that N° 8. acquired by congelation a bluiſh colour, not unlike that which the dephlogiſticated nitrous acid, in Mr. Mc NAB's former experiments, acquired by dilution with ſnow. It is not ſaid, how long the acid retained this colour, but it was intirely gone when the phial arrived in England. I am quite at a loſs to account for this phænomenon, and why it happened to this bottle only.

N° 12. when cooled to $-17°$ ſeemed to contain many icy particles; but as it afterwards bore to be cooled to $-48°$, without their increaſing, we may conclude, that they were not frozen ſpirit of nitre, but only ſome heterogeneous matter ſeparated from it. A little of the congealed part of N° 8. dropped into it while at this point, made it freeze, and it roſe to $-39°$.

In all the foregoing acids the ice was heavier than the fluid part, and in conſequence ſubſided to the bottom; a proof that it was the ſpirituous congelation which had taken place in them: but in N° 13. the frozen part ſwam at top, which ſhews, that the congelation was of the aqueous kind.

It may appear remarkable to thoſe who read Mr. Mc NAB's experiments, that theſe acids bore to be heated ſo much above their freezing points before the ice intirely diſſolved. N° 6. bore to be heated 18 degrees, N° 7. 13 degrees, and N° 12. 17 degrees above their freezing points, before all the congealed acid had diſappeared. But as, in order to diſſolve this congealed matter, they were brought into a room in all probability a great many degrees warmer than the points to which they were heated, ſo that the liquors heated faſt; and as during the diſſolution the ice would ſubſide to the bottom; it is not extraordinary, that the fluid part in the phial might be many degrees warmer than the frozen part, unleſs the phials were much agitated during the time, which nothing ſhews them to have been; eſpecially if we conſider the great quantity of heat which, in all probability, muſt be communicated to the frozen acid in order to melt it; and that, perhaps, the frozen acid may receive and part with its heat but ſlowly. It muſt be obſerved, that in N° 6. and 12. the frozen part might very likely be of a conſiderably different ſtrength, and in conſequence its freezing point might be ſeveral degrees different from that of the whole maſs, ſo that the temperature to which the fluid was heated, in order to melt the ice, might very likely not differ ſo much from the freezing point of the ice itſelf as is here ſet down. But this could not be the caſe with N° 7.

It muſt be obſerved, that when Mr. Mc NAB wanted to try the temperature of N° 7. after it had frozen in the firſt manner, the ſtopper ſtuck ſo tight that he was not able to remove it without warming it before the fire. The thermometer was then introduced, and ſtood ſeveral minutes therein at $+ 1°\frac{1}{2}$, or $+ 2°$. As the thermometer remained ſo long at this point, one

might naturally ſuppoſe, that this was the true freezing point of the unfrozen acid. But yet, from what has been juſt ſaid, it ſeems not improbable that it may be otherwiſe, and that the true freezing point may be ſenſibly lower; for which reaſon it is marked in the table with an aſteriſk (*) as doubtful.

It was before ſaid, that the temperatures in the ninth column of the foregoing table, are the freezing points anſwering to the ſtrengths expreſſed in the third column, and that $-41°\frac{1}{2}$ is the freezing point anſwering to the ſtrength of ,561; whence the freezing points determined by theſe experiments, and their reſpective ſtrengths, are as follows:

Strength.	Freezing point.
	°
,561	−41,6
,445	− 3,8
,390	− 4
,353	−11
,343	−13,8
,310	−23
,276	−40,3

By interpolation from theſe *data*, according to NEWTON's method †, it appears, that the ſtrength at which the acid freezes with the leaſt cold is ,418, and that the freezing point anſwering to that ſtrength is $-2°\frac{4}{10}$.

In order to ſhew more readily the freezing point anſwering to any given ſtrength, I have computed, by the ſame method, the following table, in which the ſtrengths increaſe in arithmetical progreſſion.

† Princip. Math. Lib. III. prop. 40. lem. 5.

Strength.

Strength.	Freezing point.	Difference.
,568	−45,5	
		+15,4
,538	−30,1	
		+12
,508	−18,1	
		+ 8,7
,478	− 9,4	
		+ 5,3
,448	− 4,1	
		+ 1,7
,418	− 2,4	
		− 1,8
,388	− 4,2	
		− 5,5
,358	− 9,7	
		− 8
,328	−17,7	
		−10
,298	−27,7	

It was before ſhewn, that the freezing points, found by the firſt method, ought to be below thoſe of the whole maſs, and muſt, in all probability, be above thoſe of the decanted liquor. In order to ſee how this agrees with obſervation, I computed in the above-mentioned manner the freezing points anſwering to the ſtrength of the whole maſs, and compared them with the obſerved freezing points. The reſult is given in the following table.

N°	Strength of the whole maſs.	Strength of the decanted liquor.	Computed freezing point of the whole maſs.	Obſerved freezing point.	
				In firſt method.	In ſecond method.
7	,439	,445	− 3,2	+ 1,7	− 3,8
8	,407	,390	− 2,6	− 3,5	− 4,
9	,393	,353	− 3,7	− 4,5	−11,
10	,357	,343	−10,	−12,5	−13,8
11	,320	,310	−19,9	−22,5	−23,
12	,283	,276	−35,6	−39,1	−40,3

It

It may be obſerved, that the freezing point of N° 7. tried in the firſt way, is conſiderably above that correſponding to the ſtrength of the whole maſs; but as this experiment was ſhewn (in p. 173.) to be doubtful, and not unlikely to exceed the truth, we may ſafely reject it as erroneous. All the others, as might be expected, are lower than thoſe correſponding to the ſtrength of the whole maſs, and above thoſe obſerved in the ſecond manner, and therefore ſerve to confirm the truth of the above determination of the freezing points of ſpirit of nitre; and alſo ſhew, that in this acid the point of ſpirituous congelation is pretty regular, and does not depend much, if at all, on the rapidity with which the congelation is performed.

The point of aqueous congelation, however, ſeems liable to conſiderable irregularity; for N° 13. after having been expoſed to the cold, froze on agitation, the congelation, as was before ſaid, being of the aqueous kind, and the thermometer ſtood ſtationary therein at $-34°$. The ice being then almoſt melted, it was again expoſed to the cold, till a good deal was frozen; but yet its temperature was then no lower than $-32°\frac{1}{4}$, though the quantity of frozen matter muſt certainly have been much more than in the firſt trial. The fluid part being then decanted, and the frozen part melted, both were again expoſed to the cold. They both were made to congeal by agitation, and the temperature of the undecanted was then found to be $-35°$, and that of the decanted part $-37°$: ſo that it ſhould ſeem as if the freezing point found by the haſty congelation was always lower than that found the other way, which may, perhaps, proceed from this cauſe; namely, that when ſufficient time is allowed, the watery part will ſeparate from the reſt, and freeze in a degree of cold much leſs than what is

required to produce that effect, when it is performed in a more rapid manner.

Theſe experiments confirm the truth of the concluſions I drew from Mr. Mc NAB's former experiments; for, firſt, there is a certain degree of ſtrength at which ſpirit of nitre freezes with a leſs degree of cold than when it is either ſtronger or weaker; and when ſpirit of nitre, of a different ſtrength from that, is made to congeal, the frozen part approaches nearer to the foregoing degree of ſtrength than the unfrozen. Likewiſe this ſtrength, as well as the freezing point correſponding thereto, and the freezing point anſwering to the ſtrength of ,54, come out very nearly the ſame as I concluded from thoſe experiments; for by the preſent experiments they come out ,418, $-2°\frac{4}{10}$, and $-31°$, and by the former ,411, $-1°\frac{1}{2}$, and $-31°$. But the freezing point anſwering to the ſtrength of ,38 is totally different from what I there ſuppoſed. This muſt have been owing to the ſtrength of that acid having been very different from what I thought it; which is not improbable, as its ſtrength was inferred only from the quantity of ſnow which was added to it in finding the degree of cold produced by its mixture with ſnow.

After the foregoing experiments were finiſhed, Mr. Mc NAB made ſome more for determining the freezing points both of the decanted and undecanted part; but for want of a ſufficient explanation of the manner in which they were executed, I have not been able to make any uſe of them. In their preſent ſtate they ſhew much appearance of irregularity; but this would very likely have been cleared up, if the circumſtances had been more fully detailed.

On the Vitriolic Acid.

An irregularity of a remarkable kind occurred in trying two of theſe acids; namely, when the undecanted part was melted and again made to congeal, its freezing point was found to be much leſs cold than that of the decanted part, and the difference was much greater than could be attributed to the difference of ſtrength. This ſeems to have happened only in the two ſtrongeſt acids, namely, N° 1. and 2. and in great meaſure confirms the ſuppoſition which I formed from Mr. Mc Nab's former experiments, that the congealed part of oil of vitriol differs from the reſt, not merely in ſtrength, but alſo in ſome other reſpect, which I am not acquainted with. It ſhould ſeem, however, that this property does not extend to weak oil of vitriol.

It perhaps may be ſuſpected, that this property takes place in the nitrous acid alſo, and was the cauſe of the ſlow melting of the ice taken notice of in p. 172. But I think it more likely, that that phænomenon proceeded from the cauſes there aſſigned.

Some ſmaller irregularities occurred in trying the vitriolic acid, the cauſe of which I believe was, that when this acid has been cooled below the freezing point, and begins to freeze, the congelation proceeds but ſlowly; ſo that a conſiderable time elapſes before it riſes to the true freezing point. Something of the ſame kind ſeems to take place in the nitrous acid alſo, though in a leſs degree; for the decanted liquors uſually continued to freeze and depoſit a ſmall quantity of ice, for a few minutes after they were poured off, though their cold, at leaſt in ſome inſtances, was found rather to diminiſh during that time.

It muſt be obſerved, that ſmall ſpicula of ice always came over along with the decanted liquor; and to this, in all probability, the new-formed ice attached itſelf; for otherwiſe it is likely, that no ice would have been produced.

The following table contains the ſtrength of the acids as determined before they were ſent to Hudſon's Bay, and the quantity and ſtrength of the decanted and undecanted parts when they arrived at London, and the ſtrength of the whole maſs as computed from thence. For the ſake of uniformity, I have expreſſed their ſtrengths, like thoſe of the nitrous acid, by the quantity of marble neceſſary to ſaturate them, though I did not find their ſtrength by actually trying how much marble they would diſſolve; as that method is too uncertain, on account of the ſelenite formed in the operation, and which in good meaſure defends the marble from the action of the acid. The method I uſed was, to find the weight of the plumbum vitriolatum formed by the addition of ſugar of lead, and from thence to compute the ſtrength, on the ſuppoſition that a quantity of oil of vitriol, ſufficient to produce 100 parts of plumbum vitriolatum, will diſſolve 33 of marble; as I found by experiment that ſo much oil of vitriol would ſaturate as much fixed alkali as a quantity of nitrous acid ſufficient to diſſolve 33 of marble. It may be obſerved, that the quantity of alkali, neceſſary to ſaturate a given quantity of acid, can hardly be determined with much accuracy, for which reaſon the foregoing leſs direct method was adopted; eſpecially as the precipitation of plumbum vitriolatum ſhews the proportional ſtrengths, which is the thing principally wanted, with as great accuracy as any method I know.

N°	Strength before ſent.	Decanted part.		Undecanted part.		Strength of whole maſs.
		Quantity.	Strength.	Quantity.	Strength.	
1	,977	1375	,967	3460	,963	,964
2	,918	3915	,919	1876	,905	,914
3	,846	88	,777	4915	,850	,849
4	,758	389	,710	3795	,753	,755
				547	,803	

The undecanted part of N° 4. was divided into two parts; namely, the leſs and the more congealable part; and it is the latter whoſe quantity and ſtrength is given in the laſt line.

It is well known, that oil of vitriol attracts moiſture with great avidity; and ſome of theſe acids were much expoſed to the air during the experiments made with them, and may therefore be ſuppoſed to have attracted ſo much moiſture from the air, as might ſenſibly diminiſh their ſtrength; and this ſeems actually to have been the caſe with ſome of them. But as the bottles were well ſtopped, and as, except in one acid which was the moſt expoſed to the air, the ſtrength of the whole maſs comes out not much leſs than that determined before the liquors were ſent to Hudſon's Bay, I imagine their ſtrength could not ſenſibly alter during their voyage home; and conſequently their ſtrength, at the time the laſt obſervations were made with them, could not differ much from that here ſet down.

It would be tedious to give the experiments for determining their freezing points in detail; but the reſult is as follows. The freezing point of N° 1. tried in the firſt method, was ſomewhat above + 1°, but it is uncertain how much; that tried in the ſecond manner ſeemed − 6°½. But the freezing point of the undecanted part, after having been intirely melted, and again

expoſed to the cold, was +9°. It muſt be obſerved, that though this part was in all probability at firſt ſtronger than the decanted part, yet at the time its freezing point was tried, it ſeems to have become rather weaker than that, owing to its expoſure to the air. It was before ſaid, that the freezing point tried in the ſecond manner is that of the decanted liquor; ſo that the freezing point of the decanted part ſeems to have been 13 or 14 degrees colder than that of the undecanted part; though the difference of ſtrength, if there was any, muſt in all probability have tended to produce the contrary effect.

The freezing point of N° 2. tried in the firſt way, was −26°; and that tried in the ſecond was −30°, or 26°; but yet the freezing point of the undecanted part was 26 or 30 degrees higher, namely, at zero; a difference which could ſcarcely have proceeded from the difference of ſtrength.

The freezing point of N° 3. could hardly differ much from +42°; and that of N° 4. was about −45°.

It ſhould be remarked, that when this laſt acid, as well as N° 1. and 2. were expoſed to a great cold, a ſediment formed in them. This muſt have been of a very different nature from frozen acid, as appeared both from its texture, which was ſoft and mucilaginous to the feel, inſtead of being gritty as the frozen acid always was; and alſo from its being not much increaſed by an increaſe of cold; and therefore ſeems to have been ſome impurity ſeparated from the acid. The quantity was greateſt in N° 4.; but even in this, though it appeared great, it is likely that the real quantity was very ſmall.

Another bottle of acid, whoſe ſtrength was ,659, was ſent; but Mr. Mc NAB was not able to make this freeze.

From theſe experiments it ſhould ſeem, that the freezing

point of oil of vitriol, anſwering to different ſtrengths, is nearly as follows:

Strength.	Freezing point.
	°
,977	+ 1
,918	− 26
,846	+42
,758	−45

From hence we may conclude, that oil of vitriol has not only a ſtrength of eaſieſt freezing, as Mr. KEIR has ſhewn; but that, at a ſtrength ſuperior to this, it has another point of contrary flexure, beyond which, if the ſtrength be increaſed, the cold neceſſary to freeze it again begins to diminiſh.

The ſtrength anſwering to this latter point of contrary flexure muſt, in all probability, be rather more than ,918, as the decanted or unfrozen part of N° 2. ſeemed rather ſtronger than the undecanted part; and for a like reaſon the ſtrength of eaſieſt freezing is rather more than ,846.

Mr. KEIR found that oil of vitriol froze, with the leaſt degree of cold, when its ſpecific gravity at 60° of heat was 1,780, and that the freezing point anſwering to that degree of ſtrength was +46°; which agrees pretty nearly with theſe experiments, as the ſtrength of oil of vitriol of that ſpecific gravity is ,848, that is, nearly the ſame as that of N° 3.